STANFORD UNIVERSITY
JAN
16
1934
LIBRARY

The Uniform Positive Column of an Electric Discharge in Mercury Vapor

BY

THOMAS J. KILLIAN

STANFORD UNIVERSITY LIBRARIES

STANFORD UNIVERSITY LIBRARIES

3781
P95K

The Uniform Positive Column of an Electric Discharge in Mercury Vapor

A DISSERTATION

PRESENTED TO THE
FACULTY OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

BY

THOMAS J. KILLIAN

Accepted by the Department of Physics
June, 1929

UNIFORM POSITIVE COLUMN OF AN ELECTRIC DISCHARGE IN MERCURY VAPOR

BY

THOMAS J. KILLIAN

Reprinted from PHYSICAL REVIEW, pp. 1238-1252, Vol. 35, No. 10, May 15, 1930

446401

THE UNIFORM POSITIVE COLUMN OF AN ELECTRIC DISCHARGE IN MERCURY VAPOR

By Thomas J. Killian
The Massachusetts Institute of Technology, Cambridge, Mass.
and
The Research Laboratory, General Electric Co., Schenectady

(Received January 11, 1930)

Abstract

Uniform positive column of an electric discharge in mercury vapor. The uniform positive column was studied in a long circular cylindrical tube by means of the Langmuir probe electrode method. Measurements were made of the space potentials, random electron current densities, and the electron temperatures along the axis and across a diameter of the tube at vapor pressures ranging from 0.27 baryes to 7.13 baryes. *The mobility of the electrons* was obtained and the results interpreted in terms of the mean free path of the electrons by Langevin's expression for mobility. ($\mu = 0.75e\lambda/m\bar{v}$) These mean free paths were in fair agreement with those obtained in angular scattering experiments by other investigators. *The rate of generation of positive ions* per electron was obtained from measurements of the positive ion current to the walls and the total number of electrons per unit length of tube. With the probabilities of ionization for electrons of various velocities obtained by other observers, it is found that at vapor pressures above 1.4 baryes the ionization is accounted for by the direct impacts with neutral atoms of electrons whose velocity distribution is Maxwellian. At lower vapor pressures it seems necessary to assume the presence of a larger number of higher speed electrons than is present in a Maxwellian distribution. The ratio of the concentrations of electrons at any two points on a diameter satisfies the Boltzmann equation. As the temperature of the electrons is lowered from 38,000°K to 19,900°K by raising the pressure of the mercury vapor the energy delivered to the walls by the recombination of positive ions and electrons decreases from 48 percent to 14 percent of the total input. Since less than 0.03 percent is lost through elastic collisions of electrons and atoms the remainder of the energy goes into excitation.

I. Introduction

THE electrical conditions in an ionized gas are completely determined when the densities of the electrons and ions and their distributions of velocities are known at every point within the discharge. The velocity distributions must of course be known both in direction and magnitude. From the densities of the electrons, negative ions and positive ions, n_e, n_n, and n_p respectively, the variation of the electric field can be obtained by means of Poisson's equation. A single integration of this equation gives the field at any point while a double integration the potential at the point. The currents to and the potentials of the various electrodes and walls of the tube furnish the boundary conditions necessary for the complete solution. The current densities of the electrons and ions, I_e, I_n, and I_p, can be determined in any direction at any point from the densities of the electrons and ions and the laws of their distribution of velocities. It is not difficult to understand why

the behavior of some discharges is so complicated since any of the variables may vary in time as well as in space.

In order to gain a general idea of the mechanism of gaseous discharges an investigation should be made of the simplest sort of discharge. In the positive column conditions are primarily dependent upon the pressure and nature of the gas and the current carried by the discharge and not upon the nature and position of the electrodes and the walls of the tube. If, furthermore, the positive column be studied in a long circular cylindrical tube, conditions will not only be constant along its length but in the absence of any transverse magnetic field there will also be radial symmetry. The uniform positive column of a mercury arc was studied in such a tube by means of the Langmuir probe electrode method.[1,2,3]

The most common type of velocity distribution occurring in nature is the random type known as the Maxwellian distribution. It has been found from an analysis of the volt-ampere characteristics of small electrodes placed in the positive column of a discharge that the free electrons move with a Maxwellian distribution of velocities in nearly random directions.[1,2,4] A small electrode, placed in the discharge, will repel electrons from its neighborhood and collect positive ions when it is negatively charged. Electrons with energies greater than Ve, where V is the potential of the collector below that of the space and e the charge of an electron, can, however, reach the collector. As the potential of the collector is increased a greater number of the more slowly moving electrons will be collected. Since these electrons have a Maxwellian distribution of velocities the ratio of their concentrations in two regions differing in potential by an amount V is given by the Boltzmann equation

$$n'/n = \epsilon^{Ve/kT} \tag{1}$$

where k is the Boltzmann constant and T the temperature of the electrons. Since the velocity distribution is not affected by a retarding field the random current densities are in the same ratio as the electron concentrations. It is thus seen that the logarithm of the electron current to a small collector varies linearly with the voltage of the collector and that the rate of change of the logarithm of the electron current with respect to the voltage is e/kT, where e/k is 11,600 degrees per volt and T is the temperature of the electrons in degrees absolute. This relation is only true when the collector is negative with respect to the space. If the field is an accelerating one the current increases more slowly and according to different laws.[3] Thus there is a transition at space potential. If the probe is a small one the break may be sharp enough to fix the space potential as in Fig. 5. When the collector is at space potential there is no sheath about it and its presence does not affect the discharge. Hence the random electron current, I_e, can be obtained by dividing

[1] I. Langmuir, Jour. Frank. Inst. **196,** 751 (1923).
[2] I. Langmuir and H. Mott-Smith, Gen. Elec. Rev. **27,** 449, 538, 616, 762, 810 (1924).
[3] H. Mott-Smith and I. Langmuir, Phys. Rev. **28,** 727 (1926).
[4] I. Langmuir, Phys. Rev. **26,** 585 (1925).

the electron current to the collector at this point by the area of the collector. According to kinetic theory the density of electrons in terms of their temperature and random current is given by

$$n_e = \frac{4I_e}{ev} = \left(\frac{2\pi m}{kT}\right)^{1/2} \frac{I_e}{e} = 4.03 \times 10^{13} \frac{I_e}{T^{1/2}} \tag{2}$$

where I_e is in amperes per cm^2. There is a second method of finding the space potential which consists in analysing the electron current to a collector when it exerts an accelerating field.[2,3]

Since the fields existing in the positive column are very small the density of positive ions is very nearly equal to that of the electrons, but due to their much higher mobility the electron current is from 200 to 400 times the positive ion current.

The positive ions do not appear to have a Maxwellian distribution of velocities but seem to obtain their velocities from the fields they move through after being formed.[5] Therefore the positive ion current to a collector is a measure of the number of positive ions formed per second in a region drained by the collector and surrounded by a surface of maximum potential. This surface will be somewhat blurred due to the thermal energy of the positive ions which is probably very nearly equal to that of the gas molecules.

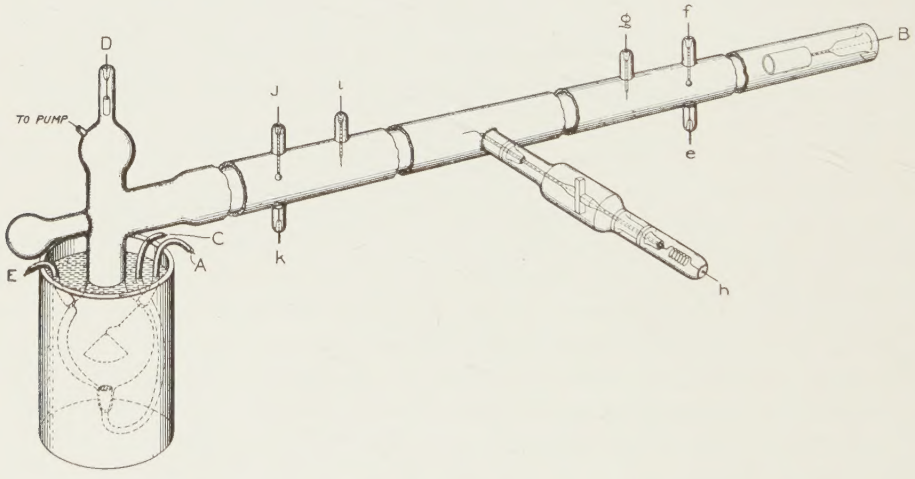

Fig. 1. Mercury vapor tube with various collectors.

II. Method

The tube used in the experiments is represented in Fig. 1. The long cylindrical portion in which the positive column was studied is 6.2 cm in diameter and 140 cm long. Anode A, which is above the pool of mercury which served as a cathode, is cone-shaped to prevent the blast of mercury from the cathode spot from affecting the pressure in the tube. Anode B consists of an

[5] L. Tonks and I. Langmuir, Phys. Rev. **34**, 876 (1929).

open molybdenum cylinder 5.1 cm long and 3.18 cm in diameter. Probe wires i and g, 61.1 cm apart, are 3 mil tungsten wires of area 0.0311 cm² each. The nickel collectors f and j, 7.6 cm respectively from g and i are approximately spherical and of area 1.22 cm² and 1.15 cm² respectively. The disks e and k bent to conform with the curvature of the walls and fitting closely against them are each of area 1.99 cm². The movable collector h consists of a 4 mil tungsten wire of 0.061 cm² area.* It can be moved by magnetic control across a diameter of the tube and also be turned to make any angle with the axis of the tube. In the present experiments it was kept parallel to the axis of the tube.

Before any experiments were made the electrodes were heated by means of a high-frequency coil and the tube allowed to run several days with a large current while being exposed to the radiation of several radiant heaters in order to drive out any water vapor or other occluded gases which might be present. Throughout all of the experiments the tube was being constantly exhausted by means of a two-stage Langmuir condensation pump and the vacuum was always such that a distinct click might be heard when the mercury was slowly raised in the McLeod gauge. The vapor pressure of the mercury in the tube was controlled by means of a water bath about the cathode bulb. When the temperature of the bath was above that of the room, mercury was prevented from condensing in the tube by means of small heating coils on each of the appendices and by exposing the whole tube to the radiant heaters.

In order to insure stable operation resistances were places in series with A and with B. In all of the runs the current to A was held between 4 and 5 amperes. Sometimes a small current was drawn to D but the effect of this upon the stability was negligible. Complete voltage current characteristics were taken of each of the collectors at various vapor pressures. At each of these vapor pressures complete characteristics were made with h at different points across the tube.

Large rectangular coils, placed above and below the tube, furnished a means of obtaining a transverse magnetic field. The effects of this transverse field upon the positive column were studied and will be reported in a later paper. In the present experiments the current through the coils was only such as to cancel the effect of the earth's field.

III. Experimental Results

Complete runs were made with the water bath about the cathode at 1.4°C, 18.6°C and 38.6°C. Using the methods of Langmuir and Mott-Smith[2] the random electron currents, electron densities and temperatures, and the

* After these experiments and others involving much higher current densities had been carried out, it was found that the probe wire h had been sputtered so that it varied from 0.0028 inches in diameter at one end to 0.004 inches at the bend into the glass tube. Since the experiments which would cause the most severe sputtering were performed after most of the runs reported here were made it is believed that the area of this probe wire was very close to 0.061 cm² when these runs were made.

space potentials were obtained from the semi-log plots of the electron current to the collector and the voltage of the collector for the probe wires i, g and h. Due probably to the small thickness of the sheaths about the probe wires better results were obtained by this method of analysis than from an analysis of the electron currents to the probe wires when they exert an accelerating field and the current to them is limited by orbital motion. In most of these runs the drift current through the tube, i_z, was held at 5 amperes. With smaller currents the agreement of the results obtained by each of the methods was very good. In each case the electron current to the collector was found by adding to the observed current the positive ion current to the collector at this voltage. This positive ion current was found by extrapolating to higher

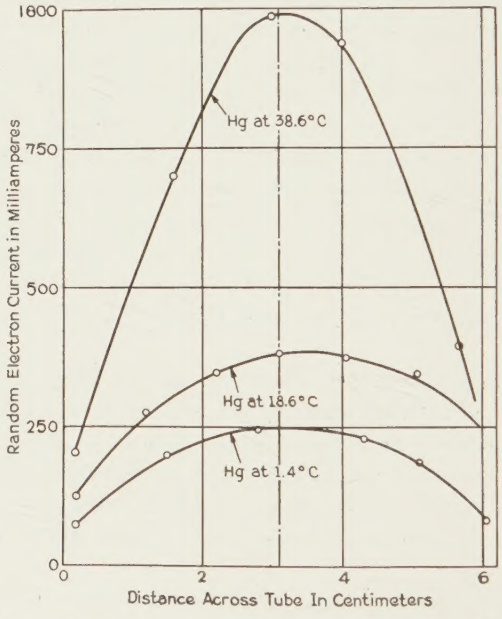

Fig. 2. Variation of the random electron current across the tube at different vapor pressures. Drift current, 5 amperes.

voltages the positive ion currents obtained at voltages so low that practically no electrons were collected.[2]

The vapor pressure of mercury was found from the data of Knudsen[6] and also that of Poindexter.[7] Since he has taken Knudsen's values at 0°C the values are very similar in the range here considered.

The positive ion current densities to the walls of the tube were obtained by plotting $(i_+)^{1/2}$ against $\nu^{1/2}$ where i_+ is the positive ion current to one of the disk-shaped collectors and $\nu = V^{3/2}\,[1+0.0247(T/V)^{1/2}]$. Here V is the voltage of the collector below that of the space and T is a factor which takes into account the initial velocities of the positive ions on entering the sheath and is about 10,000. If the positive ions had a Maxwellian distribution, T

[6] Knudsen, Ann. d. Physik **29**, 179 (1909).
[7] F. E. Poindexter, Phys. Rev. **26**, 859 (1925).

would correspond to their temperature in degrees absolute. Values of the shape factor equal to 1.36 ± 0.17 agreeing fairly well with the values Langmuir and Mott-Smith[8] found were obtained over a thirty-fold range in vapor pressure.

In Fig. 2 the variation of the random electron current across the tube is represented as measured by h. It is seen that there is a large variation

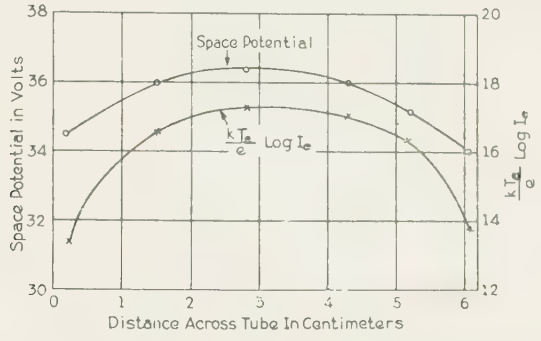

Fig. 3. Comparison of space potential with kT_e/e log I_e. Cathode bulb at 1.4°C. p, 0.264 baryes.

in this random current. In Figs. 3 and 4 are the space potentials at these points. The electrons move in a retarding field in going from the axis of tube toward the walls. If their density at any point is determined by the the Boltzmann equation the space potential curve should be identical with that of the variation of kT_e/e log I_e across the tube. It is seen that this is very

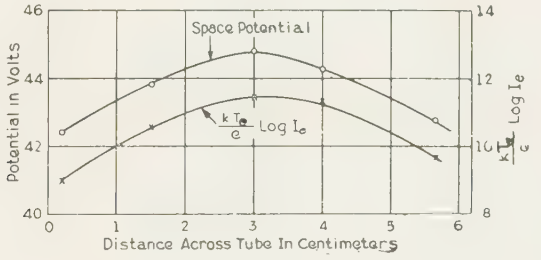

Fig. 4. Comparison of space potential curve with kT_e/e log I_e. Cathode bulb at 38.6°C. p, 7.13 baryes.

nearly true at 38.6°C. Except for the points near the walls the agreement at 1.4°C is also within the experimental error. Also the semi-log plots of the voltage-current characteristics taken at different points along the diameter should lie on the same straight line as far as the space potential, where a break occurs. This is seen to be the case in Fig. 5. Here the cathode bulb was at 38.6°C where the best results were obtained.

[8] I. Langmuir and H. Mott-Smith, Gen. Elec. Rev. **27** 541 (1924).

IV. Mobility of the Electrons

If the density of electrons at a distance r from the axis is n_e the total number of electrons per unit length of tube is

$$N_e = 2\pi \int_0^R n_e r dr \tag{3}$$

where R is the radius of the tube. If v_x is the average drift velocity of the electrons toward the anode the total electron drift current is

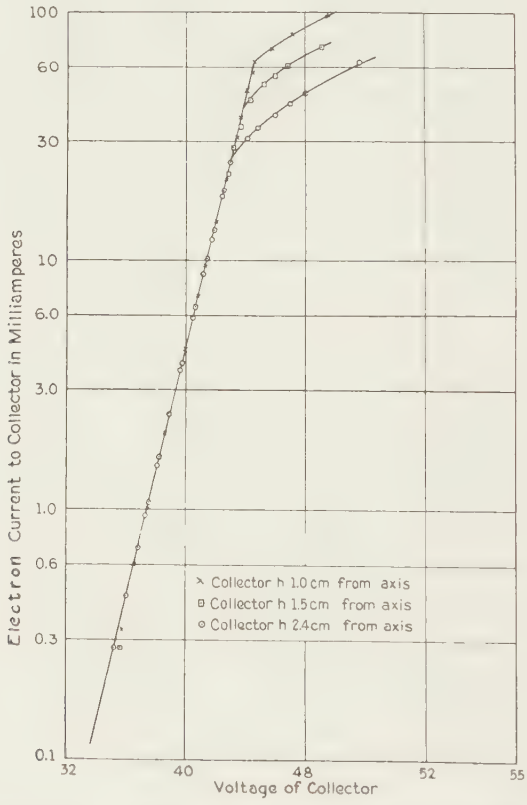

Fig. 5. Semi-logarithmic plot of the electron current to h against its voltages for various positions of h. Temperature of cathode bulb, 38.6°C. Drift current, amperes.

$$i_- = N_e e v_x. \tag{4}$$

Since the current carried by electrons is 300 or 400 times that carried by positive ions the current to the anode B, i_x, can be assumed to be equal to the electron drift current. The mobility of the electrons is given by

$$\mu_- = \frac{v_x}{X} = \frac{i_x}{N_e e X} \tag{5}$$

where X is the longitudinal potential gradient. Assuming the speed gained between successive collisions to be small compared with the average speed of the electrons Langevin[9] has derived an expression for the mobility of electrons given by

$$\mu_- = 0.75e\lambda/m\bar{v} \tag{6}$$

where λ is the mean free path of the electrons in the gas, m the mass of an electron and $\bar{v}$ the average speed.

Since $\bar{v} = (8kT/\pi m)^{1/2}$ it is possible to combine Eqs. (5) and (6) and obtain

$$\lambda = \frac{(8kTm)^{1/2} i_x}{0.75(\pi)^{1/2} N_e e^2 X} = 2.94 \times 10^9 \frac{i_x T^{1/2}}{N_e X} \tag{7}$$

where T is the temperature of the electrons in degrees absolute, i_x the drift current in amperes and X the longitudinal voltage gradient. N_e was obtained by a graphical integration of Eq. (3), n_e being found by means of Eq. (2). In Column 4 of Table I are the values of the mean free path of electrons in mercury vapor for three different vapor pressures. In reducing to λ_1, the mean free path at 1 barye and 20°C, it was assumed that the temperature of the gas molecules was 50°C. The kinetic theory value of the mean free path (i.e. $4(2)^{1/2}$ times the mean free path of gas molecules) is usually taken to be about 20 cm at this temperature and pressure.[10] Since, however, the mean free path is dependent upon the velocity of the electrons this value cannot be expected to apply very accurately.

TABLE I

Temperature of Cathode Bulb °C	Pressure of Hg baryes	T_e °K	λ from Eq. (7) cm	λ_1 cm	λ_1' from Eq. (8) cm
1.4	0.27	38,000	27.6	6.78	12.9
18.6	1.38	27,500	5.7	7.14	9.6
38.6	7.13	19,900	1.46	9.45	8.3

The angular scattering of low-velocity electrons in mercury vapor has been studied by various investigators whose results can be interpreted in terms of the mean free path of the electron.[11,12,13,14] A comparison of the temperature of the electrons in Table I, Column 3, and λ_1 in Column 5 seems to show that as the velocity of the electrons is increased there is a small increase in the effective diameter of the molecules. Minkowski[11] seems to have observed this Ramsauer effect for electrons whose velocities were less than an equivalent volt. Beuthe,[13] using the Ramsauer method, studied the absorption of low-velocity electrons and found that as the velocity decreased

[9] Langevin, Ann. de Chemie et de Physique 81, **5,** 245 (1905).
[10] S. Dushman, Hochvakuumtechnik, 1926.
[11] R. Minkowski, Zeits. f. Physik **18,** 258 (1923).
[12] L. R. Maxwell, Proc. Nat. Acad. Sci. **12,** 509 (1926).
[13] H. Beuthe, Ann. d. Physik **84,** 949 (1928).
[14] T. J. Jones, Phys. Rev. **32,** 459 (1928).

the absorption increased to a maximum at about 3 volts and then fell off to about 1/6 of this maximum value at 1 volt. Jones[14] using the Ramsauer and another method could find no evidence of this effect in mercury vapor. The results he obtained by his second method are very close to those obtained by Maxwell.[12] If the mean free path of an electron is given as a function of its velocity, i.e. $\lambda\ (v)$, then the mean free path of electrons with a Maxwellian distribution of velocities at a temperature T is given by

$$\lambda' = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty \epsilon^{-mv^2/2kT}v^2\lambda(v)dv. \tag{8}$$

Using the values of $\lambda\ (v)$ as found by Maxwell[12] and reducing the mean free paths found from Eq. (8) to the mean free path, λ'_1, at 1 barye and 20°C it is seen by a comparison of these values in Column 6 with those in Column 5 that the two vastly different methods of obtaining the mean free path give results in fair quantitative agreement, although the free paths as obtained by each method vary differently with the temperature of the electrons.

One of the assumptions made in the derivation of Eq. (6) is that the speed gained between collisions is small compared with the average speed of the electrons. This is not true at the lower vapor pressures. The average distance the electrons move in the direction of the electric field between collisions, as Compton[15] has shown is given by

$$s = \mu_- E\lambda/\bar{v} = 0.75\lambda^2 eX/m\bar{v}^2. \tag{9}$$

The average energy gained between collisions is therefore $\Delta U = Xs$ and since $\bar{v}^2 = 0.849\ c^2$ and $eU = \frac{1}{2}mc^2$ the average energy gained between collisions is

$$\Delta U = 0.441\lambda^2X^2/U. \tag{10}$$

This varies from 1.5 percent of the average energy of the electrons when the cathode bulb is at 38.6°C to 12 percent when it is at 1.4°C. However, the degree of the agreement between the values of λ_1 and λ'_1 is an indication of the extent to which the simple classical kinetic theory considerations, which underlie the Langevin mobility equation and the calculation of the free path, are applicable to this case.

V. Rate of Generation of Positive Ions

a. Experimental. If I_+ is the positive ion current density to the walls, the total positive ion current to the walls per unit length of tube is $2\pi RI_+$ and since the recombination of positive ions with electrons is negligible within the positive column, the number of ionizing collisions per electron per second is given by

$$\alpha = 2\pi RI_+/eN_e. \tag{11}$$

The values of α as obtained from Eq. (11) are in row 8 of Table II.

b. Theoretical. Consider unit length of tube containing N_e electrons with a Maxwellian distribution of velocities corresponding to a temperature T. Let the gas in the tube have a pressure p and temperature T_g. An electron of

[15] K. T. Compton, Phys. Rev. **22**, 333 (1923).

velocity v has an energy of V volts where $\frac{1}{2}mv^2 = Ve$. The probability, P, of such an electron making an ionizing collision in going unit distance is dependent only upon the velocity of the electron and the nature and density of the gas. For an electron of velocity v the probability is given by $P = P'(n/n') = P'(pT'_g/p'T_g)$ where P' is the probability of an ionizing collision per cm path at pressure p' and temperature T'_g. These probabilities have been studied for different gases including mercury vapor by Compton and Van Voorhis[16] and for mercury vapor by Jones[17] and by von Hippel.[18]

The probability that an electron of velocity v will make an ionizing collision in one second is Pv. The number of electrons whose velocities lie between v and $v+dv$ is

$$N_e f(v)dv = 4\pi N_e \left(\frac{m}{2\pi kT}\right)^{3/2} v^2 \epsilon^{-mv^2/2kT} dv. \tag{12}$$

Hence, the number of positive ions formed per second by electrons whose velocities are between v and $v+dv$ is given by

$$N_e P f(v) v dv = 4\pi N_e \left(\frac{m}{2\pi kT}\right)^{3/2} P v^3 \epsilon^{-mv^2/2kT} dv. \tag{13}$$

If v be replaced by $(2Ve/m)^{1/2}$ the number of positive ions formed per second by electrons whose energies lie between V and $V+dV$ is found to be

$$N_e P F(V) dV = 8\pi N_e \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{e^2}{m^2} P V \epsilon^{-eV/kT} dV. \tag{14}$$

In the case of mercury it has been found that the probability of ionization for electrons of less than 30 volts, varies linearly with the difference between the energy of the impinging electron and that required to ionize. Thus if V is less than V_i, P is zero but if V is greater than V_i but less than $3V_i$ we may write $P = \beta(V - V_i)$. Since, however, very few electrons have energies greater than $3V_i$ the total number of positive ions formed per second per cm is approximately

$$\nu_p = 8\pi N_e \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{e^2}{m^2} \beta \int_{V_i}^{\infty} (V - V_i) V \epsilon^{-eV/kT} dV. \tag{15}$$

Integrating this expression and dividing by the total number of electrons per unit length of tube, the number of positive ions formed per second by each electron is found to be

$$\alpha' = \beta \left(\frac{8kT}{\pi m}\right)^{1/2} \epsilon^{-eV_i/kT} \left(V_i + \frac{2kT}{e}\right)$$

$$= 6.24 \times 10^5 \beta T^{1/2} \epsilon^{-eV_i/kT} \left(V_i + \frac{2kT}{e}\right) \tag{16}$$

[16] K. T. Compton and C. C. Van Voorhis, Phys. Rev. **26,** 436 (1925); **27,** 724 (1926)
[17] T. J. Jones, Phys. Rev. **29,** 822 (1927).
[18] A. von Hippel, Ann. d. Physik **87,** 1035 (1928).

In order to find out how much Eq. (16) is in error due to the fact that Eq. (15) is integrated to infinity, Eq. (15) may be integrated from $3V_i$ to infinity and the contribution to α' of electrons whose energies are greater than $3V_i$ found. This contribution, α'_1, divided by α' gives the maximum relative error made in assuming that the expression for the probability holds to infinity. It is found that

$$\frac{\alpha_1'}{\alpha'} = \epsilon^{-2V_i e/kT}\left\{\frac{(6eV_i^2/kT)+5V_i+(2kT/e)}{V_i+(2kT/e)}\right\}. \tag{17}$$

Since $V_i = 10.4$ volts, α'_1/α' varies from 0.00018 for T equal to 20,000°K to 0.033 for T equal to 40,000°K. Thus the error made in integrating Eq. (15) from V_i to infinity is small.

From the work of Compton and Van Voorhis[16] β is given by $0.20\ p/T_0$ while from that of Jones[17] it is equal to $0.28\ p/T_0$ where p is in baryes and T_0 in degrees Kelvin. The values of α' as found by substituting these two values of β in Eq. (16) are in row 9 of Table II. It is seen that at higher vapor pressures the ionization within the positive column may be accounted for by the impacts with neutral atoms of electrons whose velocity distribution is Maxwellian. However at 1.4°C it would appear that only about 40 percent of the positive ions are produced by these electrons. At this low pressure with the mean free path of the electrons several times the diameter of the tube there is probably very little cumulative ionization.

A more acceptable explanation of the relatively large values of α found at low pressures as compared with the calculated values, is to assume that the excess ionization is due to "high-speed" electrons, not belonging to the Maxwellian group considered above. At 0.27 baryes the random current is only 4.3 times the drift current so that there are probably present more "high-speed" electrons than there would be if the electrons were moving in random directions with a Maxwellian distribution corresponding to 38,000°K.

In the experiments of Compton and Van Voorhis[16] and also in those of Jones[17] a measured current of electrons of a given speed was passed through an ionizing chamber and the number of positive ions produced measured. For electrons whose energies lay between 10 and 30 volts the effect of the fields necessary to collect the positive ions was less in the arrangement of Jones than in that of Compton and Van Voorhis.

When an electron ionizes an atom it will not only lose an amount of energy corresponding to the ionization potential but will in general divide its energy with the new electron formed. Then the average energy of the two electrons is half of the surplus energy. The impinging electron and that formed by ionization will be considered secondary electrons. The total surplus energy delivered per second to these secondary electrons is given by

$$W' = 8\pi N_e\left(\frac{m}{2\pi kT}\right)^{3/2}\frac{e^3}{m^2}\int_{V_i}^{\infty} PV(V-V_i)\epsilon^{-eV/kT}dV. \tag{18}$$

To find the average energy transferred per ionizing collision Eq. (18) is divided by the number of ionizing collisions per second and the average energy of the secondary electrons is found to be

$$\bar{V} = \frac{kT}{e}\left\{\frac{eV_i + 3kT}{eV_i + 2kT}\right\}. \tag{19}$$

If $\bar{V}_e$ is the average energy of the primary electrons ($e\bar{V}_e = 3kT/2$) the following results are obtained

$T=0$	$\bar{V}=0.667\bar{V}_e$
$T=10{,}000°\text{K}$	$\bar{V}=0.714\bar{V}_e$
$T=40{,}000°\text{K}$	$\bar{V}=0.797\bar{V}_e$
$T\rightarrow\infty$	$\bar{V}\rightarrow\bar{V}_e$

The secondary electrons would have a Maxwellian distribution of velocities if the probability of ionization were independent of the energy of the impinging electron. However, since this probability increases with the energy of the electrons there exists among the secondaries a surplus of higher-speed electrons and a deficiency of the lower-speed ones. Since the rate at which a Maxwellian distribution is reëstablished among the electrons decreases with decreasing vapor pressures[19] the discrepancies between the values of α and α' at 0.27 baryes may in part be due to this surplus of higher-speed electrons at this pressure.

TABLE II. *Summary of results. Diameter of tube =6.2 cm.*

1. Bulb temperature	°C	1.4	18.6	38.6
2. Pressure of Hg vapor	baryes	0.27	1.38	7.13
3. Drift current	amperes	5.0	5.0	5.0
4. Longitudinal potential gradient (X)	volts cm^{-1}	0.0932	0.196	0.311
5. Electron temperature (T)	°K	38,000	27,500	19,900
6. $2\pi\int_0^R n_e r\,dr$	N_e	11.1×10^{11}	21.8×10^{11}	45.7×10^{11}
7. Positive ion current density to the walls of tube (I_+)	milliamps cm^{-2}	0.356	0.45	0.505
8. Rate of production of positive ions per electron from Eq. (11)	α	41,000	25,800	13,800
9. Rate of production of positive ions per electron from Eq. (16)				
$\beta=0.20\ p_0/T_0$	α'	14,600	16,900	12,600
$\beta=0.28\ p_0/T_0$		20,400	23,600	17,600
10. Random electron current in the direction of the axis ($2\pi\int_0^R I_e r\,dr$)	amperes	21.5	35.8	64

* Tonks and Langmuir[5] derive an expression for α for a cylindrical mercury discharge at low pressures gives by $\alpha = 703.1\ T_e^{1/2}/R$. The values of α obtained by means of this expression are: at 1.4°C, 44,200; at 18.6°C, 37,500; at 38.6°C, 32,000.

VI. Energy Balance

The power input per unit length of tube is

$$W = Xi_x \tag{20}$$

[19] A. F. Dittmer, Phys. Rev. **28,** 507 (1926).

where X is as before the longitudinal potential gradient and i_x the drift current in the tube. Part of this energy is delivered to the walls by the recombination of positive ions and electrons, by the absorption of radiation and by the diffusion of metastable atoms to the walls and part goes into radiation which escapes from the tube. The total energy delivered to the walls by the recombination of a positive ion and an electron is the sum of the energy of recombination and the energies of the combining electron and positive ion. Since the electrons are moving in a retarding field their average energy expressed in volts is $2k\,T/e$. Therefore the total energy delivered to the walls per second by recombination is

$$W_r = 2\pi R I_+ (V_i + 2kT/e + \overline{V}_p) \tag{21}$$

where $\overline{V}_p$ is the average energy of the positive ions. The positive ions acquire most of their energy in the sheath close to the walls. The potential of the walls must be such as to make the current of electrons equal to that of the positive ions. It is therefore that at which zero current flows to a small collector against the walls such as e or k. The potential of a point on the axis opposite e or k can be found from the longitudinal gradient and the space potentials at i or g. Thus the difference between the potentials of points on the axis and the walls opposite can be found. Combining this with the results obtained by means of collector h as given in Figs. 3 and 4 the total variation of potential across a diameter of the tube can be found. Since the temperature of the electrons is constant the rate of production of positive ions at any point is proportional to the electron density. The energy acquired by a positive ion from the time it is formed until it recombines at the walls is equal to the difference between the potentials at the point where it was formed and that at which it recombined. At very low vapor pressures when the probability of a collision is very small it will deliver all this energy to the walls. However, even if it does make collisions and lose energy to gas molecules they in turn will deliver it to the walls. As a first approximation the longitudinal potential gradient may be neglected and the average energy delivered to the walls due to the fields the positive ions move in is given by

$$\overline{V}_p = \frac{2\pi\alpha \int_0^R n_e V_r r\,dr}{2\pi\alpha \int_0^R n_e r\,dr} = \frac{2\pi \int_0^R n_e V_r r\,dr}{N_e} \tag{22}$$

where V_r is the difference between the potentials at r and R and n_e is the electron density at r. $\overline{V}_p$ was obtained graphically from Eq. (22) and found to vary from 7.3 volts at 38.6°C to 14.5 volts at 1.4°C. The fraction of the power input delivered to the walls ($F_r = W_r/W$) by the recombining ions and electrons is in the fourth column of Table III. It is seen that this fraction increases rapidly with the temperature of the electrons.

By multiplying the frequency of collisions between electrons and gas molecules by the average loss of energy per electron per elastic collision the energy lost by the electrons per second through elastic collisions can be found.

When the energy of electrons is much greater than that of the gas molecules Compton[15] has shown that the average fraction of energy lost at an elastic collision is $2m_e/M$. Using the values of mean free paths as found from Eq. (7) and given in column 4 of Table I, the fraction, F_e, of the power input delivered by the electrons to the gas molecules by elastic collisions was found. It is seen from column 5 of Table III that this energy is very small and may be neglected.

TABLE III. *Fraction of power input delivered to the walls by the recombination of positive ions and electrons. Arc current = 5 amperes.*

Temp. of cathode bulb °C	Temp. of electrons T °K	Power input per unit length W watts	Fraction to walls F_r	Fraction to gas molecules by elastic impacts F_e
1.4	38,000	0.466	0.483	2.8×10^{-5}
18.6	27,500	0.98	0.233	4.0×10^{-5}
38.6	19,900	1.55	0.136	2.5×10^{-4}

In order to obtain a rough idea of the efficiency of excitation it may be assumed that the remainder of the energy input goes into raising the mercury atoms from the normal 1^1S_0 to the 2^3P_1 state, which excitation requires 4.9 volts. This state is between the two metastable states 2^3P_0 at 4.66 volts and 2^3P_2 at 5.43 volts. Making this assumption the average number of resonance collisions per electron per second, α_r, and per atom per second, a_r, can be found. These values are given in the third and fourth columns of Table IV. Using the values of the mean free path found by means of Eq. (7) the probability of ionization, P'_i, and that of resonance, P'_r, can be obtained. These values are given in the fifth and sixth columns of Table IV.

TABLE IV

Temp. of cathode bulb °C	Temp. of electrons °K	Number of resonance collisions per electron per second α_r	Number of resonance collisions per atom per second a_r	Probability of ionization on collision P_i'	Probability of excitation on collision P_r'
1.4	38,000	2.78×10^5	1690	0.0091	0.063
18.6	27,500	4.41×10^5	1030	0.0014	0.024
38.6	19,900	3.74×10^5	354	0.00023	0.0062

Few data are available on the probability of excitation on collision in mercury vapor. Sponer[20] found the average efficiency to be about 0.004 for the excitation of mercury atoms by electrons of from 5 to 6 volts energy. Using a different value for the total number of impacts made by the electrons Hertz[21] recalculated her results and obtained 0.03 for the average efficiency.

VII. Discussion of Results

The free electrons in the uniform positive column move in nearly random directions with a Maxwellian distribution of velocities. This distribution

[20] H. Sponer, Zeits. f. Physik **7**, 185 (1921).
[21] G. Hertz, Zeits. f. Physik **32**, 298 (1925).

is being continually disturbed by the loss of higher-speed electrons to the walls and by excitation and ionization. This continuous loss of energy by the electrons is supplied to the drift current by the longitudinal field and in some manner is transferred to the electrons so that they keep their Maxwellian distribution. No satisfactory explanation of the mechanism by which this distribution is maintained has yet been offered. There is evidence that it may be due to oscillations.[22,23] In any event it has been shown that the temperature corresponding to this distribution of velocities is one of the most important characteristics of the discharge. It determines the ionization and excitation efficiencies of the electrons. Furthermore, since the electrons have a Maxwellian distribution of velocities their concentrations satisfy the Boltzmann equation.

The mobility of the electrons was measured and by means of the Langevin equation the results were interpreted in terms of the mean free path of the electrons. Over a twenty-five fold range of vapor pressures the mean free paths found in this way, when reduced to the values at 1 barye and 20°C, were within 30 percent of each other. It was true even when the mean free path appeared to be five or six times the diameter of the tube. This is probably because the electrons make specular reflections at the walls. Their momentum is unchanged except for the component perpendicular to the walls, which is reversed.

The rate of production of positive ions seems to be accounted for by direct impacts with neutral atoms of the higher-speed electrons of the Maxwellian group when the vapor pressure is greater than 1.4 baryes. At 0.27 baryes only about one half of the ionization can be accounted for in this way. The small ratio of the random to the drift current probably accounts for the additional high-speed electrons.

It is seen that as the temperature of the electrons is lowered from 38,000° K to 19,900°K by raising the pressure the percentage of the energy delivered to the walls by the recombination of positive ions and electrons decreases from 48 to 14.

There are several sources of error in this work which are difficult to eliminate. The space potentials are probably accurate to within two-tenths of a volt. The random electron currents may be in error due to the fact that some electrons are reflected when the collector is at space potential. However, the results of Farnsworth[24] show that this coefficient of reflection must be very small under these conditions. The electron temperatures in the tube were usually within 1500°K of each other as measured by any collector during a run. It is therefore believed that the probable error is within five percent.

The author wishes to express his appreciation for the many suggestions and kind assistance of Dr. I. Langmuir and Dr. L. Tonks of the Research Laboratory of the General Electric Company at Schenectady where this work was done. He is also grateful for the considerable aid rendered by Professor K. T. Compton of Princeton University.

[22] I. Langmuir, Proc. Nat. Acad. Sci. **14,** 627 (1928).
[23] L. Tonks and I. Langmuir, Phys. Rev. **33,** 195 (1929).
[24] H. E. Farnsworth, Phys. Rev. **25,** 41 (1925).